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Synthesis, Spectral characterization and Antimicrobial studies of Metal (II) complexes with (12*E*)-*N'*-[1-(2-0x0-2*H*-chromen-3-yl)ethylidene]benzofuran carbohydrazide.

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ABSTRACT

Metal complexes of the type ML_2 . H_2O , where M = Co(II), Ni(II), Cu(II) and MLCl. H_2O where M = Zn(II), Cd(II), Hg(II) and L = OCEBFC, Schiff base derived from the condensation of benzofuran-2-carbohydrazide with 3-acetyl-2H –chromen-2-one have been synthesized. The structure of the complexes have been proposed in the light of analytical, IR, UV-Vis, ¹H NMR, FAB-Mass, ESR spectral data and magnetic studies. The complexes are soluble in DMF and DMSO. The measured molar conductance values indicate that, the complexes are non-electrolytic in nature. On the basis of these studies six coordinated dimeric octahedral structure has been assigned to Co(II), Ni(II) and Cu(II) complexes and four coordinated tetrahedral geometry to Zn(II), Cd(II) and Hg(II) complexes. The Schiff base and their metal complexes have been tested for their antibacterial and antifungal activities by Cup plate method.

Keywords: Benzofuran Schiff base, coumarin, Metal complexes, Spectral studies, Antimicrobial activity.

INTRODUCTION

Schiff's base ligands and their metal complexes plays an important role in the development of coordination chemistry, related to catalysis [1], enzymatic reactions, magnetism, molecular architectures, food industry, dye industry, analytical chemistry, bacterial, fungicidal and agrochemical activity [2]. It has long been known that, metal ions involved in biological processes of life and has been the subject of interest.

Benzofuran compounds are abundantly present in nature, particularly among the plant kingdom, often such natural products possessing benzofuran nucleus are endowed with useful pharmacological properties. Baker's yeast contains a benzofuran derivative, which acts as an antioxidant and prevents, haemorrhagin liver necrosis in rats and haemolysis of red cells in vitamin E deficient rats [3]. The seed oil of plant "Egonoki" which is much common in Japan is known to contain a benzofuran derivative called "Egonol". It is an effective synergist for rotenone pyrethrum against houseflies, mosquitoes, aphids and many other insects [4] Some benzofuran derivatives such as 2-acetylbenzofuran and 2-nitrobenzofuran are well known biodynamic agents possessing various pharmacological properties [5-7].

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Coumarin (1, 2-benzopyrone) compounds are of a large family of organic compounds having a lactone structure and extensively used in many fields. The biological activities of coumarin and related compounds are multiple and include antimicrobial [8], antioxidant, anti-inflammatory [9], antituberculosis [10], antitumour [11], spasmolytic [12], anthelmintic [13] and diuretic [14] activities.

Considering the biological importance of the above compounds, the present work deals with the synthesis and characterization of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal complexes with newly synthesized Schiff base derived from benzofuran-2-carbohydrazide and 3-acetyl-2*H* –chromen-2-one. The Schiff base and their metal complexes were tested for their antibacterial and antifungal activities.

MATERIALS AND METHODS

Experimental

All the chemicals used were of analytical reagent grade (AR), and are of highest purity available. Benzofuran-2carbohydrazide was synthesized according to the literature procedure [15]. The metal and chloride contents were determined as per Vogel's procedure [16]. Carbon, Hydrogen and Nitrogen analysis were carried out micro analytically on a Perkin Elmer 240C model at the Central Drug Research Institute (CDRI) Lucknow. The IR spectra of the Schiff base and their Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes were recorded in KBr pellets in the region 4000-350cm⁻¹ range on a Perkin Elmer 783 FT-IR spectrophotometer. The electronic spectra of the Co(II), Ni(II) and Cu(II) complexes were recorded on an Elico-SL-164 double beam UV-visible spectrophotometer in the range 200-1100nm in DMF (10^{-3} M) solution. The ¹H NMR spectra were recorded in DMSO-d₆ on a Bruker 300 MHz spectrophotometer using TMS as an internal standard. The ESR spectrum of the Cu(II) complex in polycrystalline state was recorded on a Varian-E-4X band EPR spectrophotometer using TCNE as 'g' marker (g=2.00277) at room temperature .FAB-Mass spectra were recorded on a 'JEOL SX 102 Mass Spectrometer' at CDRI Lucknow. Molar conductivity measurements were recorded on a Elico CM-180 conductivity bridge in DMF (10^{-3} M) solution using a dip-type conductivity cell fitted with a platinum electrode and the magnetic susceptibility measurements were made at room temperature on a Gouy balance using Hg[Co(NCS)₄] as the calibrant.

Synthesis of the Ligand,

(12E)-N'-[1-(2-oxo-2H-chromen-3-yl)ethylidene]benzofuran carbohydrazide

A mixture of equimolar quantities of ethanolic solution (20 mL) of benzofuran-2-carbohydrazide (0.1 mol) and ethanolic solution (20 ml) of 3-acetyl-2*H* –chromen-2-one (0.1 mol) was refluxed on water bath for about 5 hours. The product that was separated out as intense yellow coloured crystalline solid on cooling was filtered, washed with alcohol and recrystallised from ethanol (Scheme-1). Yield: 62%, m. p= 198 °C.



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General procedure for the synthesis of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes.

An ethanolic solution (20 mL) of metal chlorides *viz*. Co(II)/Ni(II)/Cu(II)/Zn(II)/Cd(II) or Hg(II) (0.01 mol) was added to an ethanolic solution (40 mL) of the Schiff's base ligand, OCEBFC (0.01 mol). The reaction mixture was refluxed for about 3 hours on water bath and then an aqueous ethanolic solution of sodium acetate was added to maintain the pH of the reaction medium about 6-7. The reaction mixture was further, refluxed for about 1 more hour. The resulting mixture was cooled and decomposed by pouring in to approximately 100 mL distilled water with constant stirring. The suspended coloured solid complexes were allowed to settle and collected by filtration, washed with sufficient quantity of distilled water repeatedly and finally with little hot ethanol and air-dried (yield: 60-65%).

Antibacterial and antifungal assays

The biological activities of synthesized Schiff base and their Co(II), Ni(II),Cu(II), Zn(II), Cd(II) and Hg(II) complexes have been studied for their antibacterial and antifungal activities respectively in DMF solvent. The Antibacterial activity of test compounds was assessed against *Staphylococcus aureus* (gram-positive) and *Escherichia coli* (gram-negative) organisms and antifungal activity against *Aspergillus niger* and *Aspergillus flavus* by cup-plate zone inhibition technique [17]. Accurately weighed 10 mg of test compound was dissolved in 10 mL of dimethylformamide in serially labeled sterilize test tubes, from the stock solution 0.1mL (100 μ L) of solution was used for antimicrobial assay.

Antibacterial assay

The Nutrient agar prepared by dissolving bacteriological peptone (1g/L), Beef extract (5g/L), Sodium chloride (5g/L) in distilled water and the pH of the solution was adjusted to 7.4 by sodium hydroxide (1M) or hydrochloric acid (1M). This solution was filtered and agar (20g/L) was added. Then it was sterilized for 15 min at 15 lb/kg pressure.

About 15-20 mL of molten nutrient agar was poured into each of the sterilized petri dishes of 3.5 inches diameter, with the help of sterile cork borer two cups of each with 8mm diameter were pouched and scooped out the set agar (two cups were numbered for the particular test compounds). The agar plates so prepared are divided into two sets and each set of the plates were inoculated with the suspension of particular organisms by spread plate techniques. The cups of inoculated plates were then filled with 0.1 mL of the test solution, the plates were allowed to stay for 2 hrs in refrigerator further the plates were incubated at 37°C for 24 hrs. The zone of inhibition developed if any, was then measured for the particular compound with particular organisms.

Norflaxin (20 mg/mL) was used as a standard and DMF control was also put to know the activity of the solvent.

Antifungal assay

The media used for antifungal activity was the potato-dextrose agar. It was prepared as follows, potato pieces (120g) were dissolved in 10mL distilled water by steaming for 30 min. the solution was filtered while hot and the volume was made up to 400 mL. To this solution dextrose (4g) and agar (8 g) were added and dissolved by steaming for 30 min. The so formed potato-dextrose agar (PDA) media was poured into two separated conical flasks and were separately inoculated with above fungus using sterile metal wire loop.

About 15-20 mL of molten potato-dextrose agar was poured into each of the sterilized petridishes of 3.5 inches diameter with the help of sterile cork borer, two cups of each with 8 mm diameter were punched and scooped out from the set PBA medium (two cups were numbered for the particular test compounds). The plates so prepared are divided in to separate sets of plates, were inoculated with the suspension particular organism by spread plate technique.

The cups of inoculated plates were then filled with 0.1 mL of the test solution the plates were allowed to stay there, as they are in their upright position for two hrs. Further the plates were incubated at 37° C for 72 hrs. The zone of inhibition developed, if any was then measured for the particular compound with particular organism.

Chlorometazole (20 mg/mL) was used as a standard. DMF control was also put to known the activity of the solvent.

RESULTS AND DISCUSSION

All the complexes are light colored, are soluble in DMF and DMSO and sparingly soluble in common organic solvents. The elemental analysis indicate that the metal complexes of Co(II), Ni(II) and Cu(II) posses the 1:2 type of stoichiometry with the empirical formula $[ML_2]$.H₂O The Zn(II), Cd(II) and Hg(II) complexes posses 1:1 type of stoichiometry with the empirical formula [MLC1].H₂O. The molar conductance values (18.21-10.58) Ohm⁻¹ cm² mole⁻¹ is too low to account for any dissociation of the complexes in DMF, indicating non-electrolytic nature of the complexes [18] (Table 1).

				^a M.P.		^b Elen	iental An	alysis			
Ligand / Complexes	Emp. Formula/ Mol. formula	Colour	Mol. Weight	°C [Yield %]	%С	%Н	%N	%М	%Cl	${}^{c}\mu^{e\!f\!f\!.}$	$^{d}\Lambda$
[OCEBFC]	$C_{20}H_{14}N_2O_4$	Pale Yellow	346.34	198 [70]	69.00 (69.36)	4.10 (4.07)	8.20 (8.09)				
Co(II) Complex	$\begin{array}{l} [Co(C_{20}H_{13}N_2O_4)_2].H_2O\\ C_{40}H_{28}N_4O_9Co \end{array}$	Brown	767.61	>300 [76]	62.20 (62.59)	3.68 (3.43)	7.30 (7.51)	7.68 (7.37)		4.90	13.54
Ni(II) Complex	$[Ni(C_{20}H_{13}N_2O_4)_2].H_2O\\C_{40}H_{28}N_4\ NiO_9$	Light Brown	766.12	>300 [70]	62.54 (62.61)	3.40 (3.68)	7.55 (7.30)	7.10 (7.65)		3.01	15.22
Cu(II) Complex	$[Cu(C_{20}H_{13}N_2O_4)_2].H_2O \\ C_{40}H_{28} CuN_4O_9$	Light Green	772.22	>300 [68]	62.50 (62.21)	3.40 (3.65)	7.50 (7.26)	8.48 (8.23)		1.93	17.85
Zn(II) Complex	$\begin{array}{l} [Zn(C_{20}H_{13}N_{2}O_{4})Cl].H_{2}O\\ C_{20}H_{15}ClN_{2}O_{5}Zn \end{array}$	Yellow	464.19	292 [70]	51.50 (51.75)	3.50 (3.26)	6.40 (6.03)	14.50 (14.09)	7.50 (7.64)	Dimag	12.80
Cd(II) Complex	$[Cd(C_{20}H_{13}N_2O_4)Cl].H_2O \\ C_{20}H_{15} CdClN_2O_5$	Yellow	511.21	296 [65]	46.50 (46.99)	2.50 (2.96)	5.50 (5.48)	21.50 (21.99)	7.00 (6.94)	Dimag	18.21
Hg(II) Complex	$[Hg(C_{20}H_{13}N_2O_4)Cl].H_2O\\C_{20}H_{15}ClHgN_2O_5$	Light Yellow	599.39	>300 [75]	40.50 (40.08)	2.00 (2.52)	4.20 (4.67)	33.00 (33.47)	5.55 (5.91)	Dimag	10.58

Table-1. Analytical and Physico-Chemical data of the Schiff's base ligand [OCEBFC] and its Metal Complexes

^aMelting point/Decomposition Temperature, ^bFound (Calculated), ^cBM/ M^{2+} ion and ^dMolar conductance Ohm⁻¹ cm²mol⁻¹ of 10⁻³M sol^a in DMF

IR spectral studies

The infrared spectral study of metal complexes gives valuable information about the nature of metal ligand bond, molecular symmetry, electronic distribution and stability of the complexes. The interpretation of IR data of the ligand and its complexes are presented in table 2. The band in the region 3235 and 1660 cm⁻¹ in free ligand are assigned to amide v(NH) and v(C=O) stretching vibrations respectively. The disappearance of these two bands in the IR spectra of the complexes shows the enolistion of amide carbonyl function and the subsequent coordination of oxygen of the enolised carbonyl with metal ion through the deprotonation. This fact of enolistion of amide carbonyl during complexation was further confirmed by appearances of new sharp band in the region 1612-1600 cm⁻¹ in these complexes which has assigned to characteristic of azine (-C=N-N=C-) moiety [19, 20] of the coordinated ligand. In the present study high intensity sharp band observed at 1709 cm⁻¹ is assigned to v(C=O) of lactone. The Shifting of this band to lower wave number side in the complexes indicates the bonding through oxygen of lactone v(C=O)group and they become weak in all the complexes. This indicates the coordination of lactone oxygen to the metal ion [21] in all complexes. The Schiff base shows the band at 1569 cm⁻¹ due to v(C=N) vibration [22]. This band in complexes shifts to lower frequency side and appear in the region 1549-1557 cm⁻¹ indicating involvement of azomethine nitrogen in bonding with metal ions. The medium to strong intensity bands observed in the region 1110-1150 cm⁻¹ is attributed to v(C-O-C) stretching vibration of benzofuran ring in the free ligand [23]. This band shows no shift in the complexes suggesting non-participation of 'O' of v(C-O-C) group. The band observed at 1272-1265 cm^{-1} is assigned to v(C–O–C) of chromane ring vibration [24] remain unperturbed and appeared in the region 1275 cm⁻¹ rules out the possibility of coordination through oxygen atom of the lacton ring of chromane moiety of all the complexes.

Ligand/Complex	v(H ₂ O)/(N-H)	$^{a}v(C=O)/^{b}(C=O)$	v(C=N)	v(N-N)	v(M-O)	v(M-N)
[OCEBFC]	3235	1709/1660	1569	1024		
Co(II) - Complex	3412	1685	1550	1030	540	429
Ni(II) - Complex	3427	1690	1557	1033	538	430
Cu(II) - Complex	3423	1686	1552	1026	542	431
Zn(II) - Complex	3420	1684	1550	1037	549	429
Cd(II) - Complex	3423	1688	1549	1030	540	428
Hg(II) - Complex	3443	1685	1552	1029	538	428

Table-2. The important IR bands of the Schiff's-base ligand [OCEBFC] and its Complexes in cm⁻¹

^{*a*}v(C=O) for lactone and ^{*b*}v(C=O) for amide

In view of these assignments the non–ligand weak intensity bands observed in the complexes in the region 431-428 cm⁻¹ are assigned to v(M-N) stretching vibrations in all the complexes and the bands in the region 549-538 cm⁻¹ are assigned to v(M-O) stretching vibrations in the present study, in all the complexes. In the present investigation, the v(M-Cl) stretching vibrations are sensitive to the oxidation state and coordination number of central metal ion and 1218

useful in predicting the stereochemistry of the complexes, on the basis of above discussion we assigned ν (M–Cl) stretching vibrations in the region 321-315 cm⁻¹.



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¹H NMR spectral studies

¹H NMR spectra of Schiff base and its Zn(II) complex were recorded in DMSO- d_6 . (Fig 1 and 2). The ligand OCEBFC showed a fine signal at δ 11.70 (s, 1H) due to amide proton [CONH]. The azomethine proton has appeared at δ 9.10 (s, 1H) as a singlet. Ten aromatic protons of benzofuran nucleus and phenyl rings have resonated in the region δ 6.90-8.95 (m, 10H) as a multiplet. The singlet appeared at δ 3.50 (s, 3H, –NC-CH₃) due to methyl protons of methyliminomethyl functional group. In Zn(II) complex of ligand the azomethine proton has shifted from δ 9.10 to δ 9.40 due to coordination of N atom with the metal ion. The amide proton has disappeared due to enolistion indicating the coordination of amide –CO group. Thus ¹HNMR spectral observations supplement the assigned geometry.

MASS SPECTRAL STUDIES

The mass spectrum of the ligand [OCEBFC] is depicted in Fig. 3. The spectrum exhibited a M^+ peak at m/z 346, which matches with the molecular mass of the ligand. This on probable fragmentations leads to the cleavage of amide boding to yield fragments almost equal to mass unit exhibit a peak at m/z 145 (M^+ -C₉H₅O₂, 20%). This supports the formation of expected Schiff's base, when benzofuron-2-carbohydrazide was reacted with 3-acetly-2*H*-chromen-2-one.



ELECTRONIC SPECTRAL STUDIES

The electronic spectra of the Co(II), Ni(II) and Cu(II) complexes were recorded in freshly prepared DMF solution (10⁻³M) at room temperature and their spectral data are presented in Table-3. The electronic spectra of Co(II) complex show bands at 16528 and 20618 cm⁻¹. These two bands are assignable to ${}^{4}T_{1g}$ (F) $\rightarrow {}^{4}A_{2g}$ (F) (v₂) and ${}^{4}T_{1g}$ (F) $\rightarrow {}^{4}T_{2g}$ (F) (v₃) transitions respectively in an octahedral environment [25]. The v₁ band could not be observed, however, v₁ band would be calculated using an equation suggested by Underhill and Billing [26]. The Ni(II) complex exhibit two absorption bands at 15748 and 25974 cm⁻¹ assignable to ${}^{3}A_{2g}$ (F) $\rightarrow {}^{3}T_{1g}$ (F) (v₂) and ${}^{3}A_{2g}$ (F) $\rightarrow {}^{3}T_{1g}$ (P) (v₃) transitions respectively in an octahedral environment. The lowest band v₁ could not be observed due to limited range of the instrument used. However, it is calculated by using band fitting procedure [26]. The Cu(II) complex exhibit a single broad asymmetric band in the region 12658–17094 cm⁻¹. The broadness of the band indicates the three transitions ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ (v₁), ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ (v₂) and ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ (v₃) which are similar in energy and give rise to only one broad absorption band. The broadness of the band may be due to dynamic Jahn–Teller

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distortion. All of these data suggest a distorted octahedral geometry around Cu(II) ion. The octahedral geometry [27] is further supported by the values of ligand field parameters such as Racah inter-electronic repulsion parameter (B), ligand field splitting energy (10 Dq), covalency factor (β) and ligand field stabilization energy (LFSE) [28]. The B values for the complexes were lower than free ion values, which is an indication of orbital overlap and delocalization of d – orbitals. The β values obtained are less than unity suggesting a considerable amount of covalent character for the metal–ligand bonds. The β value for Ni(II) complex is less than the Co(II) complex, indicating more covalency of M – L [29].

Table-3 Electronic spectral bands and ligand field parameters of the Co(II), Ni(II) and Cu(II) complexes in DMF (10⁻³M) solution

Complexes	Transitions in cm ⁻¹			Dq (cm	$B' (cm^{-1})$	β	β%	v_2 / v_1	LFSE
	v_1^a	V2	V3	1)					(k.cal)
[Co(C ₂₀ H ₁₃ N ₂ O ₄) ₂].H ₂ O	7868	16528	20618	866	903	0.9299	7.003	1.247	14.845
[Ni(C ₂₀ H ₁₃ N ₂ O ₄) ₂].H ₂ O	9900	15748	25974	990	801	0.9519	4.807	1.649	33.942
$[Cu(C_{20}H_{13}N_2O_4)_2].H_2O$	12658-17094		1487	-	-	-	-	25.491	

^aCalculated values

MAGNETIC PROPERTIES

The magnetic moments obtained at room temperature are listed in Table-1. The magnetic measurements for Co(II) and Ni(II) complexes showed magnetic moment values of 4.90 and 3.01 BM, respectively suggesting consistency with their octahedral environment [30-32]. The Cu(II) complex show magnetic moment value of 1.93 BM expected for one unpaired electron, which offers possibility of a distorted octahedral geometry [33].

ESR SPECTRUM OF THE Cu(II) COMPLEX

The ESR spectra of Copper(II) complex in a polycrystalline state has been recorded at room temperature. The g_{\parallel} and g_{\perp} values have been found to be 2.204 and 2.050 respectively. The g_{av} was calculated to be 2.1026. The spectra have asymmetric bands with $g_{\parallel} > g_{\perp} > 2.00277$ observed, indicating the unpaired electrons lie predominantly in the d_{x2-y2} orbital with possibly mixing of d_{z2} orbital because of low symmetry [34]. The axial symmetry parameter 'G' is determined as $G = (g_{\parallel} - 2.00277) / (g_{\perp} - 2.00277) = 4.26$ is found to be more than 4 suggesting very weak interaction or no interaction in the solid state [35].

ANTIBACTERIAL AND ANTIFUNGAL ACTIVITIES

The results of the antibacterial activity for the ligand OCEBFC and its complexes showed weak activity 10-14 mm inhibition (Table 4, Figs 4 and 5) against *E. coli* and *S. aureus*, whereas Hg(II) complex showed moderate activity i.e. 14 and 13mm growth inhibition against the same organisms when compared to the standard drug Norflaxin which showed 22mm and 24mm growth inhibition against *E. coli* and *S. aureus* respectively. Results of the antifungal activity of the ligand OCEBFC and its metal complexes revealed that the ligand showed moderate activity against *A. niger* and *A. flavus* with 14mm and 13mm growth inhibition against both fungi and rest of the complexes showed moderate activity with 10-13mm inhibition against *A. niger* and *A. flavus* respectively when compared with standard drug Chlorometazole.

Table-4 Antibacterial and Antifungal activity results of the Ligand OCEBFC and its metal complexes (Zone of inhibition in mm)

Compound	E. coli	S. aureus	A. flavus	A. niger
OCEBFC	10	11	14	13
Co(II) -Complex	11	10	11	11
Ni(II) - Complex	10	10	13	13
Cu(II) -Complex	12	11	13	12
Zn(II) - Complex	12	10	14	14
Cd(II) -Complex	11	11	10	13
Hg(II) -Complex	14	13	14	15
Norflaxin	22	24		
Chlorometazole			20	22
DMF(control)				
Bore size	08	08	08	08

The biological activity of any compound or complex is the combination of steric, electronic and pharmacokinetic factors. A possible explanation for the toxicity of the complexes has been postulated in the light of chelation theory [36]. It was suggested that the chelation reduces considerably with the charge of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible π -electron delocalization over the whole chelate ring. This increases the liophillic character of metal chelate which favour its permeation through lipid layer's of fungus membranes. Furthermore, some fraction of the compounds may involve the formation of a

hydrogen bond through the (-N=C-) group of the chelate or the ligand with the active centers of the fungal cell constituents resulting in the interferences with the normal cell process.



Fig- 4. Antibacterial results of Schiff base [1] and Co(II) [2], Ni(II) [3], Cu(II) [4], Cd(II) [5], Zn (II) [6], Hg(II) [7] complexes and Norflaxin (Std) [8] Where B = E. coli, C = S. aureus





CONCLUSION

The bonding of ligand to metal ion is confirmed by the analytical, spectral and magnetic studies. Some of the complexes have higher antibacterial and antifungal activity than the ligand. However, biological activities are less than standards. All these observations put together lead us to propose six coordinated dimeric octahedral structures to Co(II), Ni(II) and Cu(II) complexes and tetrahedral structures to Zn(II), Cd(II) and Hg(II) complexes (Fig 6 and 7).



Where M= Co(II), Ni(II) or Cu(II) Fig- 6. Proposed structures for Co(II), Ni(II) or Cu(II) complexes



Where M= Zn(II), Cd(II) or Hg(II) Fig- 7. Proposed structures for Zn(II), Cd(II) or Hg(II) complexes

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